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Title of the invention

PROTECTION AGAINST THE OXIDATION OF COMPOSITE MATERIAL PARTS  
CONTAINING CARBON AND PARTS THUS PROTECTED

5 Background of the invention

The invention relates to providing parts made of composite material containing carbon with protection against oxidation, and in particular parts made of thermostructural composite material comprising carbon fiber reinforcement densified by a matrix that is constituted at least in part by carbon.

Thermostructural composite materials are characterized by their good mechanical properties and by their ability to conserve those properties at high temperatures. Nevertheless, in an oxidizing medium, this ability to conserve good mechanical properties at high temperature depends on the presence of effective protection against oxidation. Whatever the way in which such materials are prepared, they inevitably present residual internal pores that are open and that give oxygen in the surrounding medium access to the core of the material.

In addition, in certain applications, in particular brake disks of carbon/carbon (C/C) composite material as used in aviation, the protection against oxidation must continue to be effective even in the presence of oxidation catalysts (present in the anti-icing substances used on runways) and also in the presence of moisture (landing and taxiing on wet runways).

To this end, it is well known to use protections based on aluminum phosphate, or more generally based on metal phosphates alone or in combination, such as aluminum and zinc phosphates. Deposition on the parts to be protected must be controlled in terms of quantity and geometrical distribution, for example in order to avoid applying the protective composition on certain areas of parts such as the friction surfaces of brake disks where the presence of a protective composition could harm tribological properties. A wetting

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agent is advantageously used to encourage in-depth penetration of the protective composition, which agent is applied beforehand or mixed directly with the protective composition, and the composition is applied like paint. Reference can be made, for example, to the following documents: US 5 853 821, EP 0 747 334, EP 0 677 499, and EP 0 606 851.

The effectiveness of such composition is nevertheless limited above a certain temperature threshold, at around 1000°C, at which temperature the active components of the composition decompose.

In order to improve ability to withstand higher temperatures, it is possible to combine metal-phosphate based protections against oxidation with diffusion barriers that oppose oxygen gaining access to the composite material at high temperatures, such as healing vitreous phases or sealed outer layers, e.g. outer layers of silicon carbide (SiC) obtained by chemical vapor deposition (CVD), or by applying a liquid composition containing silicon carbide in suspension, or containing a precursor for silicon carbide (such as a resin of the polycarbosilane (PCS) type which becomes transformed into silicon carbide by heat treatment). Nevertheless, the process of forming complete protection against oxidation then becomes much more complex, since the protection is constituted by two superposed layers, each requiring its own specific implementation process.

#### Objects and summary of the invention

An object of the invention is to provide a method enabling parts made of composite material containing carbon to be protected against oxidation, the method being easy to implement and being effective even in the presence of oxidation catalysts, in the presence of moisture, and when exposed to high temperatures, greater than 1000°C.

This object is achieved by a method comprising applying an impregnation composition containing at least one metal phosphate in solution, in which method, in accordance with the

invention, a composition is applied that also contains titanium diboride.

In known manner, titanium diboride  $TiB_2$  behaves as a reservoir for very progressive formation of oxides such as  $TiO_2$ ,  $B_2O_3$  which are capable of conferring to the protection against oxidation a barrier characteristic against diffusion of oxygen from the surrounding medium, thereby enabling high temperatures to be withstood, i.e. temperatures above  $1000^\circ C$ , and typically up to  $1400^\circ C$  or higher.

Above all, by associating with the element phosphorus P present in the composition and with a metal Me coming either from the phosphate precursor used or from exposure to a catalyst for oxidizing carbon and coming from the outside,  $TiB_2$  is capable of forming complex oxides of the Ti-O-P-Me type. Forming such oxides thus enables the oxidation catalyst coming from the outside to be trapped in the form of a glass, i.e. above  $1000^\circ C$ . The glass formed in this way also contributes to the oxygen diffusion barrier effect up to at least  $1400^\circ C$  while being insoluble in water, i.e. while enabling stable protection to be obtained in a moist medium.

The titanium diboride is advantageously present in the impregnation composition in the form of a powder, e.g. having mean grain size lying in the range 0.1 micrometers ( $\mu m$ ) to 200  $\mu m$ .

The impregnation composition may include solid refractory fillers other than titanium diboride, preferably fillers other than borides, for example silica, alumina, clay, in particular kaolin, or talc fillers, advantageously in powder form.

The metallic phosphate(s) contained in the impregnation composition may be selected from aluminum, zinc, and magnesium phosphates.

Typically, the impregnation composition may comprise:

- 20% to 70% by weight metal phosphate(s);
- 5% to 50% by weight titanium diboride;
- 20% to 50% by weight water; and

• 0% to 40% by weight solid fillers other than titanium diboride.

The impregnation composition is advantageously applied like paint, e.g. using a brush or spraying.

5 A preliminary step may be performed of treating the composite material part by impregnating it with an aqueous solution of a wetting agent, and then drying the aqueous solution so as to confer on the composite material wettability that is increased by the presence of the wetting agent.

10 According to another implementation feature of the method, it may include a step of applying a solution of at least one metal phosphate without any solid filler, prior to applying the composition containing at least a metal phosphate in solution together with titanium diboride, and possibly  
15 other solid fillers. Because of its smaller viscosity, the solution that does not have any solid filler, and in particular does not have any titanium diboride, can penetrate more deeply into the residual open internal pores of the composite material. As a result, the protection against  
20 oxidation comprises one or more metal phosphates anchored in depth in the pores of the composite material and an association of metal phosphate(s), titanium diboride, and possibly other solid fillers closer to the surface of the composite material.

25 Another object of the invention is to provide a composite material part containing carbon and protected against oxidation.

This object is achieved by a part provided with protection against oxidation comprising at least a metal  
30 phosphate and titanium diboride.

The protection against oxidation may additionally comprise refractory solid fillers other than titanium diboride.

35 According to a feature of the invention, the protection against oxidation presents a titanium diboride content that is higher in a portion situated close to the surface of the part

than in a portion that is deeper below the surface of the part. Thus, the protection against oxidation may not include any titanium diboride in its portion furthest from the surface of the part.

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#### Brief description of the drawings

Other features and advantages of the invention appear on reading the following description given by way of non-limiting indication and made with reference to the accompanying  
10 drawings, in which:

Figure 1 is a flow chart showing an implementation of the method of the invention;

Figure 2 shows a variant of the Figure 1 method; and

Figures 3 to 12 are graphs showing mass loss from  
15 samples of C/C composite material provided or not provided with protection against oxidation in accordance with the invention and subjected to oxidation testing under various conditions.

#### Detailed description of implementations of the invention

The invention applies to parts made of carbon-containing composite material, i.e.: parts formed by fiber reinforcement densified by a matrix, in which the reinforcing fibers and/or the matrix are constituted at least in part by carbon.  
25 Typically, the parts are C/C composite material parts or parts made of a composite material having carbon fiber reinforcement and a matrix that is a ceramic matrix or that is a combined carbon and ceramic matrix. Examples of such parts include brake disks, in particular disks for aircraft brakes.

30 Preparing composite material parts of this type comprises forming a fiber reinforcing structure and densifying it with a matrix. Densification may be performed by a liquid method, i.e. by impregnating the reinforcing fibers with a liquid composition containing a precursor for the matrix, e.g. a  
35 composition containing a resin, and then transforming the precursor by heat treatment. Densification may also be

performed by a gas method, i.e. by chemical vapor infiltration (CVI).

Whatever the method of preparation used, the resulting composite material presents residual internal open pores, i.e. a set of pores that are in communication with one another within the thickness of the material.

Putting protection against oxidation into place by impregnation with a liquid composition then consists in forming a coating in the accessible pores of the composite material down to a certain depth below the surface of the part to which the composition is applied.

In the implementation of Figure 1, a first stage of the method consists in performing in-depth treatment of the part with an aqueous solution that penetrates into the open pores of the material (step 10), the solution containing a wetting agent or surfactant. After drying (step 20), the wetting agent present on the surfaces of the pores in the material imparts increased wettability thereto.

Such a preliminary stage of in-depth treatment of a part is described in above-cited document US 5 853 821.

It is advantageous to use a wetting agent that is soluble in water and that is non-ionic, such as an oxyethylene fatty acid, an oxyethylene fatty alcohol, an oxyethylene alkyl phenol, or a higher polyol ester. The wetting agent is added to water at a concentration that preferably represents 0.05% to 5% by weight of the water so as to ensure that the aqueous solution conserves fluidity, enabling it to penetrate easily into the core of the material.

The preliminary treatment of the part may also be performed for the purpose of cleaning the composite material. For this purpose, the part can be immersed, for example, in an ultrasound vessel containing the wetting agent in aqueous solution.

After the preliminary treatment, a first impregnation step 30 can be performed on the composite material part using an aqueous solution of at least one metal phosphate, without

the addition of any solid filler, and in particular without the addition of titanium diboride. One or more phosphates are used preferably selected from aluminum, zinc, and magnesium phosphates. The content by weight of the phosphate(s) in the solution preferably lies in the range 20% to 70%.

The following step 40, which may be performed before or after drying the metal phosphate aqueous solution, consists in impregnating the part again, but using a composition containing at least one metal phosphate in aqueous solution together with titanium diboride  $TiB_2$  in powder form. At least one metal phosphate is used selected from the group constituted by aluminum, zinc, and magnesium phosphates.

In addition to  $TiB_2$ , further solid refractory fillers may be added to the impregnation composition. These fillers contribute in particular to filling in the pores of the composite material. The additional refractory fillers preferably do not include borides. They may be selected from powders of silica, aluminum, kaolin, clay, and talc.

Typically, the impregnation composition contains, in percentage by weight, 20% to 70% metal phosphate(s), 5% to 50%  $TiB_2$ , 20% to 50% water, and 0% to 40% additional solid fillers.

In order to conserve the ability to impregnate the composite material in depth, the mean grain size of the  $TiB_2$  powder preferably lies in the range 0.1  $\mu m$  to 200  $\mu m$ . The same applies to the grain sizes of the powder(s) forming the additional solid fillers.

The aqueous solution in step 30, and then the impregnation composition in step 40 can be applied to the surface of the composite material part under atmospheric pressure, e.g. by being painted on with a brush or by being sprayed on. There is no need to have recourse to higher pressures or a vacuum in order to force the impregnation composition to penetrate deeply under the effect of a pressure difference. In addition, the impregnation composition can easily be applied selectively on certain portions only of the

part. With brake disks, this makes it possible to avoid applying the protection against oxidation to the friction faces, since otherwise the protection might harm tribological behavior.

5 Step 30 may be repeated several times consecutively, as can step 40.

After step 40, a drying step is performed, e.g. in an oven in air, at a temperature of up to about 350°C (step 50).

10 After drying, the part is subjected to heat treatment in an oven under an inert atmosphere, e.g. a nitrogen atmosphere (step 60), thereby enabling the active compound for providing protection against catalytic oxidation of the carbon to be formed. The heat treatment is implemented by raising the temperature up to about 700°C to 900°C.

15 It should be observed that the preliminary stage (step 10, 20) and the step 30 are optional. Nevertheless, the preliminary stage can ensure that the material is impregnated to the core. Step 30 serves to ensure that protection against oxidation based on phosphate(s) is present in depth in the  
20 material, with it being more difficult for the impregnation composition used in step 40 to penetrate to the core of the material because of the higher viscosity of this impregnation composition. A part is thus obtained which is protected against oxidation with protection that presents a higher  
25 titanium diboride content in a portion that is situated close to a surface of the part than in a portion that is further away from the surface of the part. The protection against oxidation that is put into place may even be completely lacking in titanium diboride or additional solid fillers in  
30 its portion that is furthest from the surface of the part.

In a variant (Figure 2), after the preliminary treatment stage (steps 10 and 20), impregnation is performed (step 30') using a composition that contains at least one metal phosphate in aqueous solution, together with titanium diboride.

35 The  $TiB_2$  content in the impregnation composition is nevertheless preferably small so as to make in-depth



penetration possible. Typically, the impregnation composition comprises, in percentages by weight, 20% to 70% metal phosphate(s), and 5% to 30%  $TiB_2$ , with the remainder being water. For the same reason, the  $TiB_2$  powder is selected to have mean grain size that is quite small, for example less than 100  $\mu m$ .

The method is then continued by steps 40, 50, and 60 of impregnation, drying, and heat treatment that are similar to the steps of the method of Figure 1.

The examples given below show that the presence of  $TiB_2$  leads to a clear improvement in the behavior in an oxidizing medium of parts that are protected in accordance with the invention, in comparison with the state of the art as illustrated in particular by document US 5 853 821, when exposed to high temperatures (1000°C or more), in the presence of moisture and in the presence of catalysts for oxidizing carbon.

The Applicant believes that in addition to forming  $B_2O_3$  and  $TiO_2$  by oxidation in use, the presence of  $TiB_2$  makes it possible, by associating with the element P and the metal Me coming from the phosphate(s) or an oxidation catalyst that might be present, to form complex Ti-P-O-Me oxides that are capable, above about 1000°C, of taking over the protective action of the metal phosphate(s), even in a moist medium, firstly by trapping the oxidation catalysts, and secondly by contributing to the oxygen diffusion barrier effect provided by the simple oxides  $B_2O_3$  and  $TiO_2$ .

It should also be observed that these properties do not appear to occur with borides other than  $TiB_2$ , such that using or adding borides other than  $TiB_2$  as additional refractory solid fillers appears to be rather undesirable.

#### Example 1

Samples of C/C composite material were made as follows.

Unidirectional fiber sheets of carbon precursor fibers (preoxidized polyacrylonitrile) were superposed in different

directions and bonded together by needling as the superposition was being built up. The resulting fiber preform was subjected to heat treatment to transform the precursor into carbon by pyrolysis, and was then densified with a pyrolytic carbon matrix by chemical vapor infiltration. Such a method is well known. Reference can be made, for example, to document US 4 790 052. Samples in the form of rectangular blocks having dimensions of 20 mm x 25 mm x 8 mm were cut out from the block of C/C material obtained in this way.

Several samples were provided with protection against oxidation by a process comprising the following steps:

a) preliminary treatment of the samples by immersing them in an ultrasound vessel containing an aqueous solution of a wetting agent based on polyethoxyl isononylphenol available from the German supplier Hüls under the name "Marlophen NP9", the wetting agent being present in the solution at a concentration of 5% by weight. After impregnation, the samples were dried in an oven, leaving the pores of the composite material lined with wetting agent;

b) using a paintbrush to apply to the faces of the samples an aqueous solution containing 50% by weight aluminum dihydrogenphosphate  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , the remainder being water, such a solution being sold in France in particular by the supplier Europhos under the name "Phosphate aluminique" (aqueous solutions of  $\text{Al}(\text{H}_2\text{PO}_4)_3$  are available from other suppliers, in particular the German supplier Chemische Fabrik Budenheim KG);

c) after a few minutes, and before drying the  $\text{Al}(\text{H}_2\text{PO}_4)_3$  solution, a paintbrush was used to apply on the faces of the samples an aqueous solution containing 35% by weight of  $\text{Al}(\text{H}_2\text{PO}_4)_3$  and 44% by weight of  $\text{TiB}_2$  powder having a mean grain size equal to about 10  $\mu\text{m}$ , the remainder being water;

d) drying in air in an oven with temperature being raised slowly up to 350°C (about 1°C/min) with pauses of 5 hours (h) at 90°C, 3 h at 150°C, 1 h at 220°C, and 1 h at 350°C; and

e) heat treatment in an oven under a nitrogen atmosphere implementing the following cycle:

raising temperature up to 300°C at a rate of about 5°C/min;

5 raising temperature from 300°C to 700°C at a rate of about 2°C/min; and

a pause of 5 h at 700°C.

Samples protected in this way by a method in accordance with the invention were subjected to the following respective oxidation tests, each test being performed on three samples:

10 I) an oxidation cycle comprising exposure to air at 650°C for 5 h, return to ambient temperature and "pollution" by immersion in an aqueous solution containing 5% by weight potassium acetate, the remainder being water, and four

15 oxidation cycles by successive exposures to air at 650°C for 5 h, with intermediate returns to ambient temperature (where potassium acetate is a catalyst for oxidizing carbon and a common ingredient of anti-icing compositions used on runways);

20 II) a test similar to test I) but with oxidation cycles comprising exposure to air at 850°C for 30 min;

III) an oxidation cycle by exposure to air at 650°C for 5 h, exposure to air at 1000°C for 1 h, pollution by immersion in an aqueous solution of potassium acetate (at 5% by weight), and two successive oxidation cycles by exposure to air at

25 650°C for 5 h;

IV) an oxidation cycle by exposure to air at 650°C for 5 h, exposure to air at 1200°C for 20 min, pollution by immersion in an aqueous solution of potassium acetate (at 5% by weight), and two successive oxidation cycles by exposure to

30 air at 650°C for 5 h;

V) test similar to test IV), but without pollution with potassium acetate;

VI) test similar to test IV), but without pollution with potassium acetate and with exposure to air at 1400°C for

35 10 min (instead of 1200°C for 20 min) after the first oxidation cycle;

VII) test similar to test IV), but replacing the step of pollution with potassium acetate by a step of immersion in tap water at ambient temperature for 24 h; and

5 VIII) test similar to test IV), but replacing the step of pollution with potassium acetate by a step of immersion in boiling water for 1 h.

10 By way of comparison, each test was also performed on three samples of the same C/C composite material but protected by the prior art method described in document US 5 853 821, i.e. a method comprising steps such as a), b) (repeated once), d), and e) as described above, i.e. omitting impregnation with a composition containing  $TiB_2$ .

15 Table I below and the curves of Figures 3 to 10 show the measured mass losses after each test as a percentage relative to the initial mass, on samples protected by a method in accordance with the invention and on reference samples protected by the prior art method.

TABLE I

Test	Relative mass loss					
	Samples protected in accordance with the invention according to Example 1			Reference protected samples		
(I) - 1 x 5 h - 650°C - K acetate pollution - 4 x 5 h - 650°	5.5%	6.9%	7.3%	6.7%	7%	8%
(II) - 1 x 30 min - 850°C - K acetate pollution - 4 x 30 min - 850°	5.2%	5.5%	7%	4.4%	6.9%	7.3%
(III) - 1 x 5 h - 650°C - 1 x 1 h - 1000°C - K acetate pollution - 2 x 5 h - 650°	9%	9.5%	14%	17.5%	18%	23%
(IV) - 1 x 5 h - 650°C - 1 x 20 min - 1200°C - K acetate pollution - 2 x 5 h - 650°	11%	12%	22%	35%	39%	56%
(V) - 1 x 5 h - 650°C - 1 x 20 min - 1200°C - 2 x 5 h - 650°	2.6%	2.6%	3.4%	9.2%	13%	13%
(VI) - 1 x 5 h - 650°C - 1 x 10 min - 1400° - 2 x 5 h - 650°	2%	3%	3.5%	11.5%	27%	43.5%
(VII) - 1 x 5 h - 650°C - 1 x 20 min - 1200°C - 24 h immersion in water at ambient temperature - 2 x 5 h - 650°	6.5%	7.5%	8%	29%	31%	37%
(VIII) - 1 x 5 h - 650°C - 1 x 20 min - 1200°C - 1 h immersion in boiling water - 2 x 5 h - 650°	7.5%	8%	9%	15.5%	26%	31%

The results of the test show that compared with the prior art under consideration, the protection against oxidation implemented using a method in accordance with the invention presents the following characteristics:

effectiveness similar in the presence of a carbon oxidation catalyst for exposure to temperatures in the range 650°C to 850°C;

effectiveness very significantly increased in the presence of oxidation catalyst after exposure to 1000°C (on average about 11% mass loss compared with 20%) and to 1200°C (on average 14% mass loss compared with 43%);

effectiveness considerably improved in the absence of oxidation catalyst after exposure to 1200°C (on average about 3% mass loss compared with 12%) and to 1400°C (on average about 3% mass loss compared with 24%, and more dispersion in the results); and

effectiveness considerably better in a moist environment (on average about 7% mass loss compared with 32% after immersion in water at ambient temperature for 24 h, and on average about 8% mass loss compared with 24% and wide dispersion of results after immersion in boiling water for 1 h).

#### Example 2

The procedure was as in Example 1, but in step c), an impregnation composition was used containing, in percentage by weight, 32% of  $\text{Al}(\text{H}_2\text{PO}_4)_3$  and 56%  $\text{ZrB}_2$ , the remainder being water.

Several samples protected using the method of Example 2 were subjected to an oxidation test identical to test V) above.

Table II below shows the relative mass losses measured on the various samples after performing the observation test (as a percentage relative to initial mass). By way of comparison, Table II shows the mass losses observed in the same oxidation

test on samples protected in accordance with Example 1 and on reference protected samples.

TABLE II

5 (Test 1 x 5 h - 650°C + 1 x 20 min - 1200° + 2 x 5 h - 650°)

Samples	Mass loss
Protected in accordance with Example 1	2.6%
	2.6%
	3.4%
Protected in accordance with Example 2	10.1%
	11.4%
	12.5%
Reference	9.2%
	13%
	13%

10 The results show that using  $ZrB_2$  as a substitute for  $TiB_2$  in the impregnation composition leads to a significant loss in the effectiveness of protection against oxidation, the protection being similar to that observed on the sample protected in accordance with the prior art.

### Example 3

15 The samples used were made of C/C composite material of the same kind as in Example 1, and they were protected against oxidation by modifying the process described in Example 1 as follows:

20 in step b), an impregnation composition was used containing, in percentages by weight: 44% of  $Al(H_2PO_4)_3$  and 14% of  $TiB_2$  in powder form having a mean grain size of about 10  $\mu m$ , the remainder being water; and

25 in step c), an impregnation composition was used containing, in percentages by weight: 34% of  $Al(H_2PO_4)_3$  and 39% of  $TiB_2$  in powder form having a mean grain size equal to about 10  $\mu m$ .

#### Example 4

The procedure was as in Example 3, but during step b) a composition was used containing, in percentages by weight: 39% of  $\text{Al}(\text{H}_2\text{PO}_4)_3$  and 28% of  $\text{TiB}_2$  in powder form having mean grain size equal to about 10  $\mu\text{m}$ , the remainder being water, and in step c), a composition was used containing, in percentages by weight: 35% of  $\text{Al}(\text{H}_2\text{PO}_4)_3$  and 44% of  $\text{TiB}_2$  in powder form having mean grain size equal to about 10  $\mu\text{m}$ .

Two samples  $E_3$  and  $E_4$  protected using the methods of Examples 3 and 4 were subjected respectively to oxidation testing identical to test IV) above.

Table III below and Figure 11 show the relative mass losses that were measured (as percentages compared with the initial mass) after performing the oxidation test, repeating the results obtained with samples  $E_1$ ,  $E'_1$ , and  $E''_1$  protected in accordance with Example 1 and the reference protected samples  $E_R$ ,  $E'_R$ , and  $E''_R$ .

TABLE III

(Test 1 x 5 h - 650°C + 1 x 20 min - 1200°C + K acetate pollution + 2 x 5 h - 650°C)

Sample $E_3$ protected in accordance with Example 3	Sample $E_4$ protected in accordance with Example 4	Sample $E_1$ , $E'_1$ , $E''_1$ protected in accordance with Example 1			Reference protected samples $E_R$ , $E'_R$ , $E''_R$		
10%	9.5%	11%	12%	22%	35%	39%	56%

It can be seen that incorporating  $\text{TiB}_2$  in the first impregnation composition containing phosphate makes it possible to obtain effective protection. Nevertheless it makes impregnation to the core more difficult.

The above examples show the clear advantage provided by using  $\text{TiB}_2$  as the source for forming oxides that are capable of performing a protected barrier function against oxygen from the surrounding medium, and capable of acting with the phosphorus and the metal (regardless of whether it comes from



the phosphate(s) used or from a carbon oxidation catalyst) to form glasses that withstand moisture and trap oxidation catalysts coming from the outside.

5    Example 5

The procedure was as in Example 1 except that in step c) a composition was used containing, by weight: 23% of  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , 37% of  $\text{TiB}_2$  powder, 9% kaolin powder, and 30% water.

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Example 6

The procedure was as in Example 1 except that in step c) a composition was used containing, by weight: 24% of  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , 39% of  $\text{TiB}_2$  powder, 5% kaolin powder, 5% aluminum powder, and 27% water.

15

Example 7

The procedure was as in Example 1 except that in step c) a composition was used containing, by weight: 25% of  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , 40% of  $\text{TiB}_2$  powder, 10% aluminum hydroxide  $\text{Al}(\text{OH})_3$ , and 25% water.

20

Example 8

The procedure was as in Example 1 except that in step c) a composition was used containing, by weight: 25% of  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , 40% of  $\text{TiB}_2$  powder, 10% zinc phosphate  $\text{Zn}_3(\text{PO}_4)_2$ , and 25% water.

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Example 9

The procedure was as in Example 1 except that in step c) a composition was used containing, by weight: 25% of  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , 40% of  $\text{TiB}_2$  powder, 10% aluminum metaphosphate  $\text{Al}(\text{PO}_3)_3$ , and 25% water.

30

Samples  $\text{E}_5$  and  $\text{E}'_5$  protected in accordance with Example 5,  $\text{E}_6$ ,  $\text{E}'_6$ , and  $\text{E}''_6$  protected in accordance with Example 6,  $\text{E}_7$ , and  $\text{E}'_7$  protected in accordance with Example 7,

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E<sub>8</sub>, and E'<sub>8</sub> protected in accordance with Example 8, and E<sub>9</sub>, and E'<sub>9</sub> protected in accordance with Example 9 were subjected to an oxidation test identical to above test V).

Figure 12 shows the relative mass losses that were measured (as percentages compared with the initial mass) for these various samples, and also for the samples E<sub>1</sub>, E'<sub>1</sub>, and E''<sub>1</sub> protected in accordance with Example 1 and the reference protected samples E<sub>R</sub> and E'<sub>R</sub>.

It can be seen that the samples protected in accordance with Examples 5 to 9 present improved ability to withstand oxidation compared with the reference samples, even if they are to some extent less good than the samples protected in accordance with Example 1. This shows that it is possible in the ambit of the invention to use inert solid fillers (kaolin, alumina) that enable cost to be kept down, and also reactive fillers (aluminum hydroxide), phosphates other than Al(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub> having anticatalyst properties (such as zinc phosphate), or even an aluminum phosphate other than Al(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub>.

The content by weight of one or more of these ingredients other than TiB<sub>2</sub>, Al(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub>, and H<sub>2</sub>O in the composition used for applying the second protected layer (step c) is preferably selected to lie in the range 0% to 40%.